

## Complex Phases in Block Copolymer Solutions

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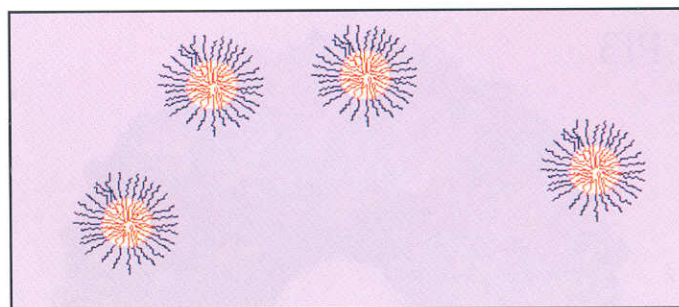
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Block copolymers are two or more chemically distinct polymers joined together. The simplest form of block copolymer is a diblock copolymer where the two polymers are joined at their ends. A triblock copolymer is shown in the diagram below.



**Figure 1:** Schematic diagram of a triblock copolymer

As such this is the next stage of complexity from a diblock. If the polymers were not joined together by a covalent bond at their ends, then at low temperature they would macrophase separate, as fat and water do in milk over time. However, since they are joined together this is prevented and microphase separation occurs [1]. In the systems that we have studied one of the blocks, the blue one (poly(oxyethylene)) is hydrophilic and the middle block, the red one, (poly(oxybutylene)) is hydrophobic. Hence, if the triblock copolymer is added to water, the poly(oxyethylene) block is solvated in the water and

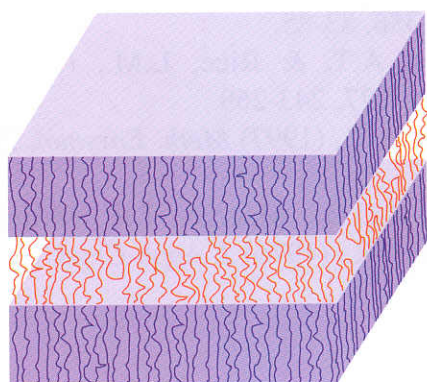


**Figure 2:** Micelles of EBE triblock copolymer in water.

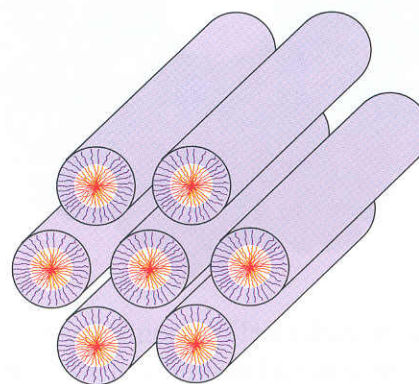
the poly(oxybutylene) block tries to curl up to prevent contact with water. If there are sufficient other triblock copolymer molecules around then the best way this can be done is for the molecules to form small spheres called micelles, where the poly(oxybutylene) blocks are on the inside away from the water and the poly(oxyethylene) are on the outside.

As the concentration is raised, the micelles aggregate and form complex structures such as fcc or hcp cubic structures, hexagonal cylinders or lamella solutions [2]. The main point of all this is that the change in structure can be brought about by changing temperature instead of changing composition as the solvent quality changes with temperature. In addition the different structures have different rheology. Thus by changing the temperature the system can change from a stiff gel that does not flow to a mobile sol that does.

We have studied three block copolymer solutions by Synchrotron SAXS and SANS. They consisted of aqueous solutions of a triblock copolymer of poly(oxyethylene)-poly(oxybutylene)-poly(oxyethylene), commonly noted  $E_nB_mE_n$ . The three triblock copolymers  $E_{16}B_{10}E_{16}$ ,  $E_{20}B_{10}E_{20}$  and



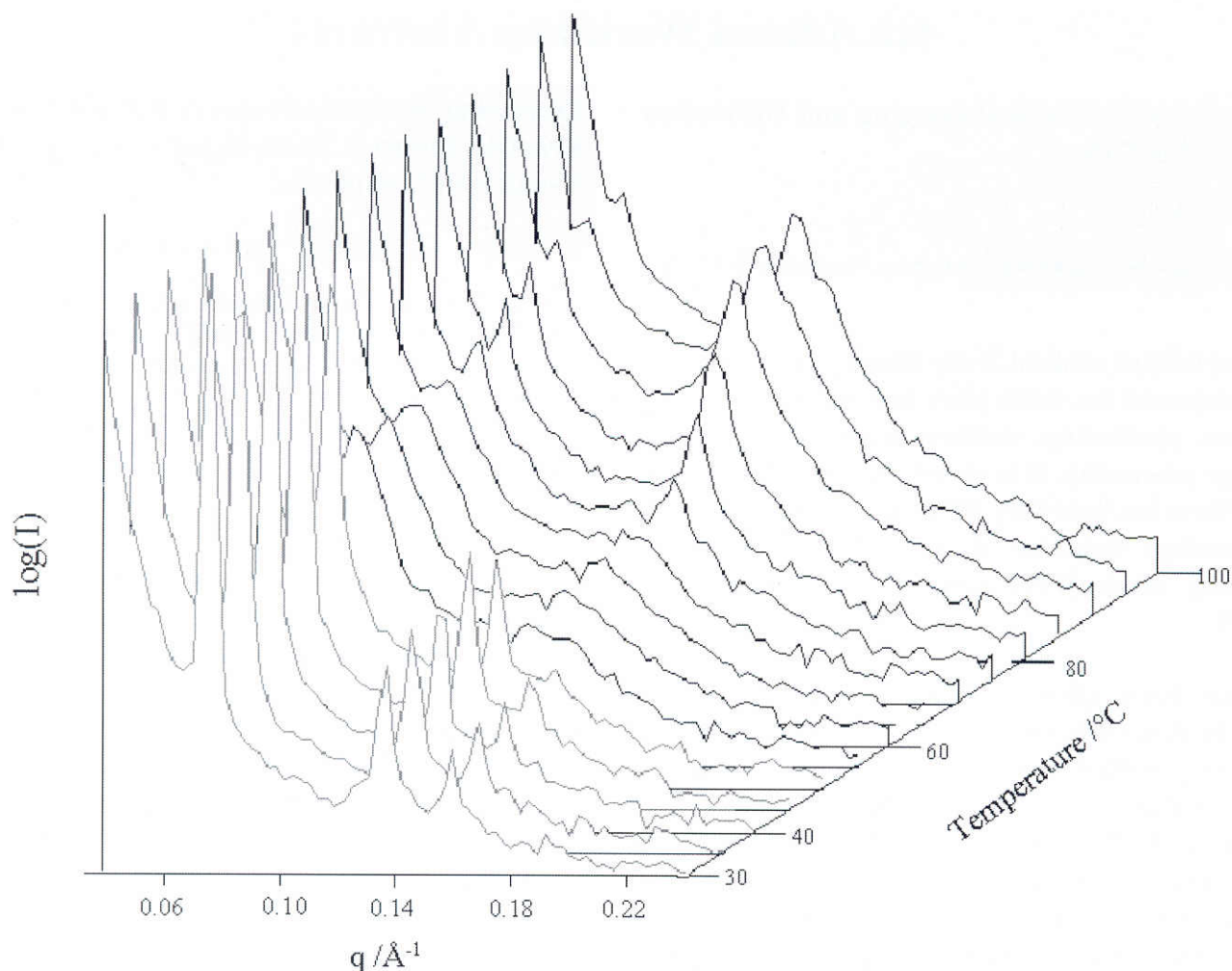
**lamella**



**hexagonal**

**Figure 3:** Lamella and hexagonal cylinder structure in water. The water is excluded from the B block areas (red).





**Figure 4:** The SAXS patterns observed during a slow heating ramp for a 45wt%  $E_{16}B_{10}E_{16}$  in water. The transition from hexagonal cylinders through disordered sol to lamella stacks can clearly be seen.

$E_{35}B_{10}E_{35}$  are readily soluble in water forming a range of phases at different compositions. It was the purpose of this study to determine the stable phases and to study their response to shear.

The initial stages of the experimental program were concerned with the temperature-morphology profile of the samples. The samples were placed in capillary tubes in a Linkam hotstage and studied by synchrotron SAXS on Station 8.2 of the Daresbury synchrotron. The temperature-morphology profile was then correlated with tube inversion and rheology studies of the materials to provide an understanding of the morphological development within them. The SAXS data clearly show the important transitions in the system from a stiff hexagonal gel to a mobile sol.

The sample  $E_{16}B_{10}E_{16}$  45wt.% shows a transition from a disordered sol below 20°C to a stiff hexagonal

gel between 20°C and 55°C, a sol again between 55°C and 65°C and is then to a lamella form up to 90°C, after which it finally disorders in to the sol. These changes are clearly represented in the scattering patterns. Such materials have commercial interest in the manufacture of inexpensive temperature sensors and in controlled drug release.

## References

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- [2] Pople, J.A., Hamley, I.W, Fairclough, J.P.A., Ryan, A.J., Komanshek, B.U., Gleeson, A.J., Yu, G-E., Booth, C., *Macromolecules*, **30**, 5721, 1997